QI² QUEST INTEGRATED, INC.

VIA U.S. MAIL

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Dr. Steven Fishman
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Office of Naval Research
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Arlington, Virginia 22217-5660

Subject: Transmittal of Progress Report for "High Strength, High Toughness In Situ Ceramic Composites," Under Contract No. N00014-95-C-0242, Data Item A001

Dear Dr. Fishman:

Enclosed, please find the subject document. It is a summary of our activities on the subject contract for the first quarter, covering November 1, 1995 through January 31, 1996.

Should you have any questions, concerns, or suggestions regarding the program, please contact me at the phone number and address listed below.

Sincerely,

Ender Savrun

Ender Savrun, Ph.D.
Director
Advanced Materials

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Enclosure

cc: G. Rogers, ONR
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HIGH STRENGTH, HIGH TOUGHNESS IN SITU CERAMIC COMPOSITES

Progress Report for the Quarter:

November 1, 1995 to January 31, 1996

Ender Savrun

Cetin Toy

Charles Henager (PNL)

February 1996

Prepared for

OFFICE OF NAVAL RESEARCH

Under Contract No. N00014-95-C-0242, Data Item A001

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Task 1: Composite Synthesis

The thermal analysis, both differential thermal analysis (DTA) and thermalgravimetric analysis (TGA), of the 3TiC+2Si (composition 32) and 3TiC+3Si (composition 33) compositions showed that solid state displacement reactions start above 1000°C in TiC-Si system. A series of pressureless sintering experiments were carried out to determine the extent of reaction in 32 and 33 compositions at 1000°C, 1300°C, and 1500°C under argon gas atmosphere. The powder mixtures were prepared by wet mixing technique as explained in the first progress report. Small 0.5 inches diameter pellet shaped samples were sintered for two hours at the predetermined temperatures. The sintered samples were analyzed by X-ray diffraction. The phases detected at each temperatrue are shown in Table 1.

Table 1: Reaction products that are formed upon sintering of 32 and 33 compositions at various temperatures.

	Phases detected in decreasing order from left to right
32 Composition	
1000°C	TiC, Si, unidentified minor peak
1300°C	TiC, Ti_3SiC_2, SiC, Si, $TiSi_2$
1500°C	TiC, SiC, unidentified minor peak
33 Composition	
1000°C	TiC, Si, unidentified minor peak
1300°C	TiC, Ti_3SiC_2, SiC, $TiSi_2$, Si
1500°C	unidentified major peaks and minor SiC

The information in Table 1 suggests that: (a) 1000°C sintering temperature is not high enough for Ti_3SiC_2 formation; (b) Ti_3SiC_2 phase may not be stable above 1500°C. Ti_3SiC_2 forms at 1300°C, however, the reaction appears to be sluggish since both compositions still contain some unreacted TiC and Si phases after 2 hours of reaction time. The sluggish nature of the reaction was thought was to be due to the lack of physical contact between the particles since no pressure was applied during the sintering. In order to test this hypothesis, a hot pressing experiment at 1300°C was performed under 31 MPa pressure to densify the samples. Composition 32 which was prepared by dry mixing at Battelle and wet mixing at QUEST, was used in this low temperature hot pressing experiment. X-ray diffraction analysis of the hot pressed samples is currently being conducted to identify the phases present. The bulk sample densities were measured and found to be lower than those obtained in the previous hot pressing experiments. The previous hot pressing schedule involved a first hot pressing at 1350°C for 2 hours, followed by a second hot pressing at 1500°C for 30 minutes. While the dry mixed batch

gave a density of 3.80 g/cm^3 (previously it was measured as 4.07 g/cm^3 after 1500°C hot pressing), the sample prepared from the wet mixed batch showed a bulk density of 3.34 g/cm^3. This result suggests that a problem occured during the wet mixing step. Either phase separation occured during mixing due to the density difference of the powders, or the powders were oxidized. The oxidation of the particles is known to slow down the displacement reaction. The cause of low densification of the two batches will be investigated in detail after determining the presence of reaction phases by X-ray diffraction and examining the resulting microstructures using light microscopy. It is most likely that wet mixing has to be revisited in detail in a follow-up Phase II program since it can potentially offer an intimate mixing of powders, which is necessary for complete reaction and densification.

A slightly lower density was also obtained from the powder batch after remixing of 32 composition by dry ball milling using AlN balls. This sample was hot pressed under 31 MPa pressure first at 1350°C for 2 hours, followed by hot pressing at 1500°C for another 30 minutes. The final sample bulk density was measured as 3.96 g/cm^3, which is lower than the previously obtained sample under similar hot pressing and heating conditions (4.07 g/cm^3). This result is also consistent with the results of low temperature hot pressing experiment mentioned above.

New 33 and 331 (3TiC+3Si+1C) composition mixtures were prepared by dry ball milling under argon gas for 16 hours by using AlN grinding balls. By dry grinding under argon gas, not only is the oxidation tendency of the particles minimized, but also the phase separation observed during the wet mixing can be avoided. The same hot pressing schedule (holding at 1350°C for 2 hours, followed by 1500°C for 30 minutes under 31 MPa) was also applied for these two new batches.

Bulk sample densities were measured as 4.09 and 3.40 g/cm^3 for 33 and 331 compositions, respectively, after the hot pressing. While a slightly higher sample density was obtained from composition 33, it was found to be a highly reactive powder mixture. There was an extensive reaction between the graphite mold and excess silicon in the batch, making it very difficult to process the composite material economically without loosing the mold and punches. Thus, it appears that hot pressing of 33 composition may not be a practical approach for the processing of Ti_3SiC_2-SiC composites. On the other hand, the addition of free carbon in 331 composition prevented the reaction between graphite die and silicon, but caused the formation of macro porosity, visible to naked eye, along the sample cross-section. The excess carbon significantly impeeds the densification of 331 composition. The amount of free carbon (C/Si = 1/3) in 331 composition appears to be high. Therefore, the amount of free carbon will be decreased to (C/Si = 1/12) in future 331 type compositions to eliminate macropore formation. X-ray diffraction analysis of these samples is currently being performed to identify the presence and the relative amount of phases present.

Task 2: Composite Characterization

Room and high temperature mechanical strength tests were performed on the (3x4x50) mm samples, prepared from the 32 Battelle composition that was reported in the first

progress report. X-ray diffraction analysis of this hot pressed sample only showed the presence of Ti_3SiC_2 and SiC phases in the microstructure. No unreacted TiC was detected. The average 4-point bend strength as a function of test temperature in air is shown in Figure 1. The highest strength obtained from these samples are around 500 MPa at 900°C. As indicated in the first progress report, examination of the microstructure by optical microscopy for this sample showed the presence of pore population larger than 50 microns in size. Since the material strength is determined by the presence of largest flaw, it is very likely that one can obtain much higher strength values at temperatures lower than 900°C if these large pores can be eliminated during the densification process. It was determined that high temperature strength decreased rapidly over 900°C. This is attributed to the increasing plastic deformation of the material with increasing temperature, as shown in Figure 2. It is expected that this high temperature plastic deformation behavior coupled with higher hot pressing pressures can be used to improve the material density and its 4-point bend strength further. Thus, a new experiment is planned to densify dry mixed 32 composition under 45 MPa pressure instead of 31 MPa that was previously used. Another significant implication of the high temperature plasticity is that the material can be hot forged into net shapes at 1000°C for many room temperature applications.

Electron microscopy of the fracture surfaces and examination of the polished cross-sections is currently being conducted of the hot pressed specimens to determine the grain size, microhardness and fracture toughness data. Wear test samples from 32 and 33 compositions are being prepared for testing at Argon National Laboratory.

Schedule

The program is on schedule without any delays. As of January 15, 1996, 30% of the project budget has been spent, and 15% is obligated.

Future Work

The following activities are planned for the next reporting period:

1. Hot press 32 composition with modified pressure profiles to enhance the densification process prior to completion of the solid state reactions.
2. Prepare mechanical and wear test specimens from 32 and 33 compositions.
3. Measure 4-point bend strength of the samples prepared from the denser 32 composition at room and elevated temperatures.
4. Characterize the microstructures using light microscopy and scanning electron microscopy.

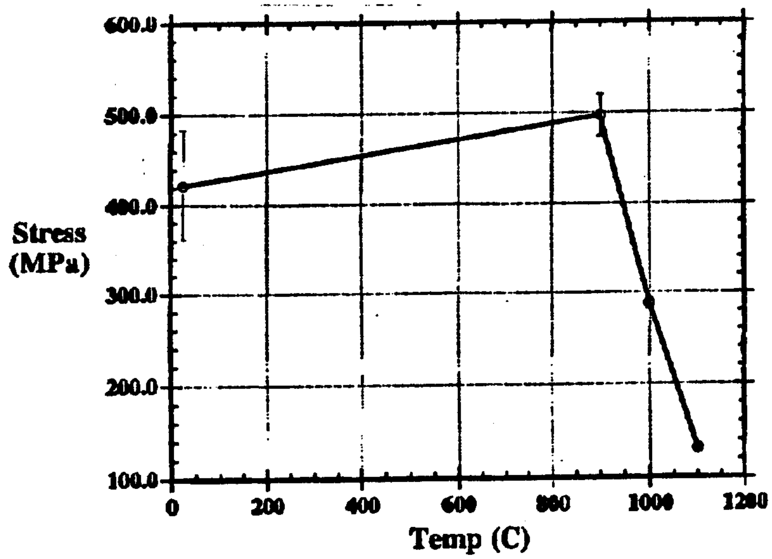

Figure 1: Four-point bend strength of the 32 composition at room and elevated temperatures.

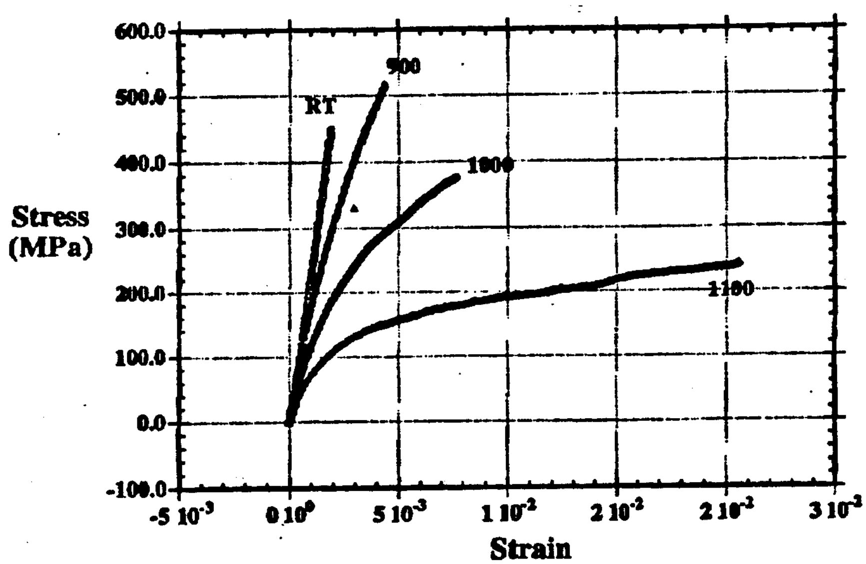

Figure 2: Stress-strain behavior of four-point bend specimens at various temperatures.